Structural and Reaction Chemistry of Tungstenocene Boryl Complexes

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The structural and reaction chemistry of $Cp_2W(H)(Bcat)$ (cat = $O_2C_6H_4$) (**1**) and Cp_2W-$(Bcat')_2$ (cat' = $O_2C_6H_3$-*t*-Bu or $O_2C_6H_2$-*t*-Bu_2) (**2a,b**) is reported. Compound **1** was prepared by reaction of the anion $[Cp_2WH]^-$ with ClBcat, and **2a,b** were prepared by oxidative addition of cat'BBcat' by photochemical or thermal generation of tungstenocene. The X-ray structures of **1** and **2a** are reported, and they display geometries indicating $d\pi-p\pi$ interaction. The reaction chemistry of these compounds with small molecules involves protonation by alcohols, water-catalyzed protonation by amines, halogenation of the hydride in **1**, and resistance toward formation of Lewis acid−base complexes. In addition, **1** undergoes photochemically induced reductive elimination of HBcat. Remarkably, generation of tungstenocene in the presence of cat'BBcat' in benzene solvent led to the formation of **2** rather than oxidative addition of the solvent.

Introduction

The chemistry of transition metal boryl compounds has been pursued recently because of the intermediacy of such complexes in transition metal-catalyzed hydroborations, the fundamental interest in electrophilic, covalently bound ligands, and the ability of a transition metal to stabilize the $^-BR_2$ reactive intermediate.[1−21] In the late 1960's and early 1970's a number of metal boryl complexes were reported,[22] although the identity of these compounds and the presence of an M−B

covalent bond has become uncertain in light of the more recent ^{11}B NMR data of crystallographically characterized examples.

We and others have recently described the structural properties of a series of metallocene boryl complexes.[5,11,23] The X-ray diffraction study of $Cp_2W(H)(Bcat)$ (**1**) (Bcat = $B(O_2C_6H_4)$) in our work provided evidence for $d\pi-p\pi$ bonding. The group 5 complexes with metal−boron bonding show an interesting combination of hydroborate and boryl structural types in the case of niobium[3] and distinct endo and exo isomers in the case of tantalum.[11] Little reaction chemistry of metallocene boryl complexes has been reported.

The formation and cleavage of B−H and B−B bonds is important in metal-catalyzed and -mediated chemistry of boranes. B−H oxidative addition is believed to be a key step in catalytic hydroboration,[1] and the oxidative addition of B−B bonds may led to metal-catalyzed diborations.[12,18,24−28] On a more fundamental level, transition metals that are not capable of cleaving C−H or C−C bonds in hydrocarbons do add the B−B bonds of diborane(4) derivatives. It is unclear if this greater reactivity for borane additions is a result of thermodynamic or kinetic effects.

We report studies on diverse reaction chemistry with a set of tungstenocene boryl compounds. This reactivity demonstrates weak boryl Lewis acidity and robust metal−boron linkages.[29] Further, we report the remarkable selectivity of the metal fragment Cp_2W for addition of B−B bonds in benzene or toluene solvent,

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1996.
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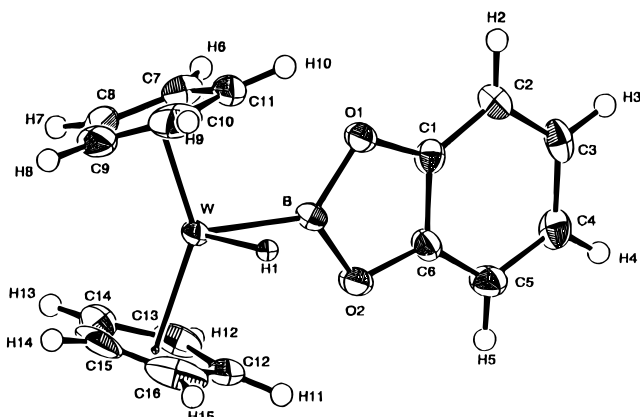(29) Rablen, P. R.; Hartwig, J. F.; Nolan, S. P. *J. Am. Chem. Soc.* **1994**, *116*, 4121.
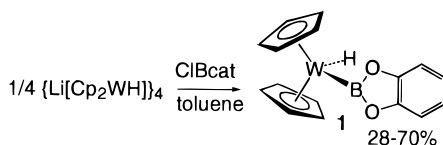
Figure 1. ORTEP drawing of **1**.

Scheme 1

$$1/4\ \{Li[Cp_2WH]\}_4 \xrightarrow[\text{toluene}]{\text{ClBcat}} \mathbf{1} \quad 28\text{–}70\%$$

which are known to react with the Cp$_2$W fragment. The structural details of a hydrido boryl and bis(boryl) complex of tungstenocene are also reported. Portions of this work have been reported in communication form.[3,5]

Results and Discussion

The formation of the tungstenocene hydrido boryl complex **1** is shown in Scheme 1. Addition of ClBcat to a slurry of the anion {Li{Cp$_2$WH}}$_4$[30] in benzene or toluene solution led to formation of the hydrido boryl compound **1** in 28–70% yield after filtration, concentration, and layering with pentane. Higher yields were obtained by crystallization from toluene/pentane mixtures at −35 °C. Crystallization from benzene/pentane at room temperature gave lower yields but led to the formation of crystals suitable for an X-ray diffraction study.

X-ray Structure of 1. Compound **1** crystallized in space group *P*2$_1$/*n*, and the structure was solved by Patterson methods. An ORTEP drawing is provided in Figure 1; tables of crystal parameters, bond distances, and bond angles are given in Tables 1–3. The structure consisted of well-separated monomeric units with no short intermolecular contacts. The overall pseudotetrahedral geometry of **1** has similar bond angles to an alkyl hydride of tungsten,[31] and the B–H distance is greater than 2 Å. Thus, no B–H interaction exists. The boryl ligand geometry is similar to those of the isoelectronic alkyl alkylidenes of tantalum.[32] The well-developed molecular orbital description of the bent metallocene fragment dictates that the carbene substituents be directed toward the Cp ligands in a sterically disfavored geometry. In order for a π-interaction between the tungsten and boryl ligand to occur, a similar geometry must be adopted. Indeed the boryl oxygens are directed toward the Cp ligands in a carbene-like geometry. Moreover, the tungsten boryl distance ap-
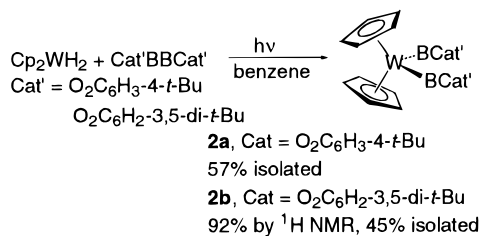
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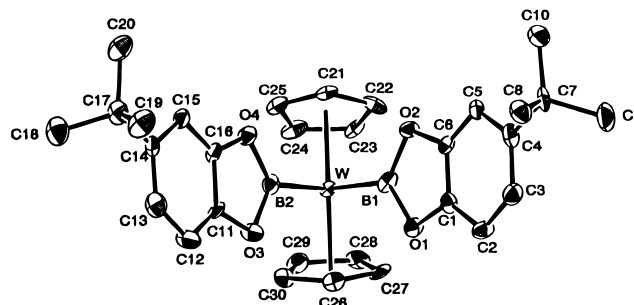(32) Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642.

Table 1. Crystal and Data Collection Parameters for 1

A. Crystal Data	
empirical formula	C$_{16}$H$_{15}$O$_2$BW
fw	433.95
cryst color	pale yellow
habit	prism
cryst dimens (mm)	0.10 × 0.20 × 0.40
cryst system	monoclinic
no. reflcns used for unit cell determinatn (2θ range (deg))	24 (30.2–38.4)
ω scan peak width at half-height	0.23
lattice param (Å, deg)	*a* = 10.118(4), *b* = 10.539(2), *c* = 13.193(2), β = 100.46(2)
V (Å^3)	1383.6(7)
space group	*P*2$_1$/*n* (No. 14)
Z value	4
D$_{calc}$ (g/cm^3)	2.083
*F*000	824
μ(Mo Kα) (cm^{-1})	85.23
B. Intensity Measurements	
diffractometer	Rigaku AFC5S
radiation (λ (Å))	Mo Kα (0.710 69)
temp (°C)	−125
attenuators	Zr foil (factors: 2.3, 5.3, 11.7)
take-off angle (deg)	6.0
detector aperture	6.0 mm hor, 6.0 mm vert
cryst to detector dist (cm)	28.5
scan type	ω-2θ
scan rate (deg/min)	8.0 (in ω) (3 rescas)
scan width (deg)	1.52 + 0.30 tan θ
2θ$_{max}$ (deg)	60.0
no. of reflcns measd	
total	4133
unique	3918 (*R*$_{int}$ = 0.078)
corrs	Lorentz-polarization, abs (transm factors: 0.73–1.00)
C. Structure Solution and Refinement	
struct solution	Patterson method
refinement	full-matrix least squares
function minimized	$\sum w(|F_o| - |F_c|)^2$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
p-factor	0.01
anomalous dispersion	all non-hydrogen atoms
no. observns (*I* > 3.00σ(*I*))	2571
no. variables	185
reflcn/param ratio	13.90
residuals: *R*, *R*$_w$	0.027, 0.028
goodness of fit indicator	1.50
max shift/error in final cycle	0.00
max peak in final diff map (e/Å^3)	0.83
min peak in final diff map (e/Å^3)	−1.17

Table 2. Bond Distances for 1[a]

W−C7	2.291(6)	C1C6	1.404(8)
W−C8	2.294(8)	C2C3	1.417(9)
W−C9	2.310(8)	C3C4	1.399(9)
W−C10	2.328(7)	C4−C5	1.391(9)
W−C11	2.280(6)	C5C6	1.390(9)
W−C12	2.288(6)	C7−C8	1.39(1)
W−C13	2.288(6)	C7−C11	1.40(1)
W−C14	2.297(7)	C8−C9	1.40(1)
W−C15	2.310(7)	C9−C10	1.41(1)
W−C16	2.326(7)	C10−C11	1.43(1)
W−B	2.190(7)	C12−C13	1.41(1)
O1−C1	1.375(7)	C12−C16	1.38(1)
O1−B	1.444(8)	C13−C14	1.41(1)
O2−C6	1.370(7)	C14−C15	1.40(1)
O2−B	1.444(8)	C15−C16	1.37(1)
C1−C2	1.381(9)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

pears shorter than predicted from a combination of covalent radii for the tungstenocene metal and boryl boron atoms. In addition to the alkyl hydride of tungestenocene, a number of Cp$_2$W−C(sp^2) bond dis-

Table 3. Selected Bond Angles (deg) for 1

Cp centroid 1–W–Cp centroid 2	144	W–B–O1	127.2(4)
Cp centroid 1–W–B	105	W–B–O2	127.1(4)
Cp centroid 1–W–H1	105	O1–B–O2	105.7(5)
Cp centroid 2–W–B	105	B–W–H	78(2)
Cp centroid 2–W–H1	101		

Scheme 2

Cp$_2$WH$_2$ + Cat'BBCat' $\xrightarrow[\text{benzene}]{h\nu}$

Cat' = O$_2$C$_6$H$_3$-4-*t*-Bu

O$_2$C$_6$H$_2$-3,5-di-*t*-Bu

2a, Cat = O$_2$C$_6$H$_3$-4-*t*-Bu
57% isolated

2b, Cat = O$_2$C$_6$H$_2$-3,5-di-*t*-Bu
92% by ^{1}H NMR, 45% isolated

tances are known.[33–35] The metal–boryl distance is similar to those of the Cp$_2$W–C(sp^2) bond lengths. Thus, the W–B distance is shortened by the difference in covalent radii between sp^2-hybridized carbon and three-coordinate boron, which is approximately 0.05– 0.1 Å.[36] This small difference alone would not support the presence of a π-interaction. However, the combination of sterically disfavored geometry and slightly shortened W–B distance suggests the presence of a weak interaction. Consistent with this interaction being weak, the unsymmetric 4-methylcatecholate version of **1** showed no hindered rotation of the boryl group by ^{1}H or ^{13}C NMR spectrometry down to −80 °C that would be detected by observation of a broadened Cp resonance. The substituted complex was prepared in analogy to the preparation of **1**, and since no variable-temperature behavior was observed, further studies with this complex were not pursued.

Synthesis of Bis(boryl) Complexes Cp$_2$W(Bcat')$_2$ (2a,b). The synthesis of bis(boryl) complex **2a,b** by oxidative addition of diboron compounds is shown in Scheme 2. Irradiation of a mixture of Cp$_2$WH$_2$ and the diboron compounds Cat'BBCat' in benzene solvent gave **2a,b** in 92% yields by NMR spectroscopy and 45−57% yields of isolated material. Photolysis of Cp$_2$WH$_2$ is known to generate the reactive intermediate Cp$_2$W, which readily inserts into aromatic C−H bonds. This intermediate does not insert into C−C bonds, and few complexes are known to add C−C bonds including those between two sp^2-hybridized C−C bonds. However, photolysis of Cp$_2$WH$_2$ in the presence of *only 1 equiv of cat'BBcat' in benzene solvent* led to the high yield formation of Cp$_2$W(Bcat')$_2$ (**2a**, cat' = 4-*t*-BuC$_6$H$_3$O$_2$B; **2b**, cat' = 3, 5-*t*-Bu$_2$C$_6$H$_2$O$_2$B). The products were isolated in analytically pure form, suitable for X-ray analysis in the case of **2a**, by concentration of the reaction solution and layering with pentane. The ^{11}B NMR chemical shifts were similar to, but shifted slightly downfield of, that for **1**. Photolysis of phenyl hydride complex Cp$_2$W(Ph)(H), the product of solvent oxidative addition, in the presence of cat'BBcat', for 3 h, did not give **2a**, demonstrating that **2a** was formed as a kinetic product. This kinetic selectivity is not simply a steri-

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Figure 2. ORTEP drawing of **2a**. Hydrogen atoms are omitted for clarity.

Table 4. Crystal and Data Collection Parameters for 2a

A. Crystal Data	
empirical formula	C$_{36}$H$_{40}$O$_4$B$_2$W
fw	742.18
cryst color/habit	pale yellow plates
cryst dimens (mm)	0.08 × 0.10 × 0.12
cryst system	monoclinic
no. reflcns used for unit cell determinatn (2θ range (deg))	25 (10.3−18.0)
lattice params (Å, deg)	$a = 14.829(4)$, $b = 7.976(2)$, $c = 27.282(5)$, $\beta = 98.76(2)$
V (Å^3)	3189(2)
space group	$P2/n$ (No. 13)
Z value	4
D_{calc} (g/cm^3)	1.546
$F000$	1488
μ(Mo Kα) (cm^{-1})	37.34
B. Intensity Measurements	
diffractometer	Enraf-Nonius CAD-4
radiation (λ (Å))	Mo Kα (0.710 69)
temp (°C)	−119
attenuator	Zr foil (factor = 20.4)
take-off angle (deg)	2.8°
detector aperture	2.0−2.5 mm hor/2.0/mm vert
cryst to detector dist (cm)	21 cm
scan type	ω-2θ
scan rate (deg/min)	1.0−16.5 (in ω)
scan width (deg)	0.53 + 1.10 tan θ
2θ$_{\text{max}}$ (deg)	52.6
no. of reflcns measd	
total	7198
unique	6929 ($R_{\text{int}} = 0.078$)
corrs	Lorentz−polarization, abs (transm factors: 0.77−1.00)
C. Structure Solution and Refinement	
struct solution	Patterson method
refinement	full-matrix least squares
function minimized	$\sum w(|F_o| - |F_c|)^2$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
p-factor	0.03
anomalous dispersion	all non-hydrogen atoms
no. observns ($I > 3.00\sigma(I)$)	4244
no. variables	388
reflcn/param ratio	10.94
residuals: R, R_w	0.041, 0.050
goodness of fit indicator	1.69
max shift/error in final cycle	0.001
max peak in final diff map (e/Å^3)	1.29
min peak in final diff map (e/Å^3)	−2.71

cally driven phenomenon, considering the lack of addition of sp^2−sp^2 C−C bonds, and most likely results from the ability of the nucleophilic Cp$_2$W fragment to coordinate to the electrophilic boron center as part of the reaction mechanism.

X-ray Structure of 2a. An X-ray diffraction study of **2a** was conducted on a sample obtained from a benzene/pentane solvent mixture. Compound **2a** crystallized in space group $P2/n$ and showed well-separated monomeric units with no intermolecular contacts. An

Table 5. Bond Distances for 2a

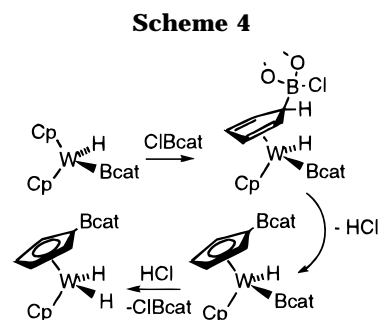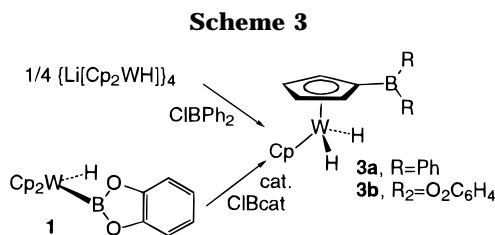|			
W−C21	2.274(8)	C5−C6	1.37(1)
W−C22	2.309(8)	C7−C8	1.55(1)
W−C23	2.295(9)	C7−C9	1.55(1)
W−C24	2.318(9)	C7−C10	1.52(1)
W−C25	2.332(8)	C11−C12	1.37(1)
W−C26	2.262(8)	C11−C16	1.38(1)
W−C27	2.301(8)	C12−C13	1.42(1)
W−C28	2.33(1)	C13−C14	1.39(1)
W−C29	2.34(1)	C14−C15	1.39(1)
W−C30	2.324(8)	C14−C17	1.54(1)
W−B1	2.19(1)	C15−C16	1.41(1)
W−B2	2.23(1)	C17−C18	1.52(1)
O1−C1	1.40(1)	C17−C19	1.54(1)
O1−B1	1.42(1)	C17−C20	1.54(1)
O2−C6	1.40(1)	C21−C22	1.42(1)
O2−B1	1.45(1)	C21−C25	1.42(1)
O3−C11	1.38(1)	C22−C23	1.40(1)
O3−B2	1.43(1)	C23−C24	1.44(1)
O4−C16	1.35(1)	C24−C25	1.43(1)
O4−B2	1.38(1)	C26−C27	1.41(1)
C12−C2	1.36(1)	C26−C30	1.41(1)
C1−C6	1.37(1)	C27−C28	1.43(1)
C2−C3	1.41(1)	C28−C29	1.44(1)
C3−C4	1.38(1)	C29−C30	1.40(1)
C4−C5	1.40(1)	C31−C32	1.35(2)
C4−C7	1.54(1)	C31−C36	1.36(3)
C32−C33	1.32(2)	C33−C34	1.34(3)
C34−C35	1.43(3)	C35−C36	1.34(3)

a Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 6. Selected Bond Angles (deg) for 2a

Cp centroid 1−W−Cp centroid 2	142	W−B1−O2	126.1(6)
Cp centroid 1−W−B1	105	O1−B1−O2	106.8(7)
Cp centroid 1−W−H2	105	W−B2−O3	124.6(6)
Cp centroid 2−W−B1	104	W−B2−O4	126.6(7)
Cp centroid 2−W−B2	105	O3−B2−O4	108.8(8)
W−B1−O1	127.0(7)	B1−W−B2	78.0(4)

ORTEP drawing is provided in Figure 2, data collection and crystal parameters are given in Table 4, and distances and angles are provided in Tables 5 and 6. The unit cell contained one benzene molecule for each tungsten complex. The two boryl ligands were oriented in a fashion that allows for π-bonding between the basic metal center and each electrophilic boryl, the same orientation as was observed in boryl hydride **1**. Of course, steric effects also strongly favor the observed geometry in **2a**. Moreover, the metal-boron distances of **2a** were similar to the M−B distances for **1**, which appeared to be shorted by π-bonding. Finally, the B−W−B angle of 78(2)° was identical to the H−W−B angle of 78(2)° and the calculated ideal angle for d^2 Cp$_2$-ML$_2$ compounds.[37] The B−M−B angles in some pseudo square planar and octahedral bis(boryl) compounds have been less than the idealized 90°,[4,12] and the angle in a recently reported Co(II) bis(boryl) was only 68°.[38] In the case of **2a**, the small B−W−B angle reflects the ideal angle of the metallocene system and does not contain any distortion, relative to the geometry of other metallocene compounds, that could be attributed to B−B interactions. Consistent with this argument, the B−B distance is 2.78(1) Å, far longer than the 1.678(3) Å B−B distance in cat′BBcat′ (cat′ = 1,2-O$_2$C$_6$H$_3$-4-*t*-Bu).[18]

Synthesis of Borylcyclopentadienyl Compounds. Scheme 3 shows reaction chemistry that forms borylcyclopentadienyl complexes. Reaction of BrBPh$_2$, which

Scheme 3

1/4 {Li[Cp$_2$WH]}$_4$ + ClBPh$_2$ → (via cat. ClBcat) **3a**, R=Ph; **3b**, R$_2$=O$_2$C$_6$H$_4$

1

Scheme 4

is more electrophilic and sterically hindered than ClBcat, with {Li[Cp$_2$WH]}$_4$[30] gave only the product of addition to the Cp-ring **3a** rather than addition to the metal center. This compound was isolated in 60% yield. Catecholboryl complex **1** was converted to a similar borylcyclopentadienyl compound **3b**, in 82% yield by addition of a catalytic amount (ca. 0.1 equiv) of ClBcat to a C$_6$D$_6$ solution of **1**. Addition of 0.1 equiv of methyl-substituted *B*-chlorocatecholborane, ClB(O$_2$C$_6$H$_3$-3-Me), led to incorporation of the methylcatecholboryl group into the rearranged product. Trace amounts of cationic tungstenocene trihydride product[39] were observed upon addition of stoichiometric quantities of ClBcat to **1**, suggesting the presence of free HCl during the reaction. Alternatively, catecholborylcyclopentadienyl complex **3b** was prepared in 21% isolated yield without isolation of the boryl intermediate **1**. Addition of 1.2 equiv of ClBcat to Li[Cp$_2$WH] followed by stirring for 2 h gave **3b**. Borylcyclopentadienyl compounds have been sought for their ability to act as a ligand-based coordination site for substrates.[40,41]

It is likely that the electrophilicity of the haloborane controls the rate of the borane-catalyzed formal migration, and the rearrangement is certainly not a simple, intramolecular migration. Rather it appears to occur by an electrophilic addition to the coordinated cyclopentadienyl ring and elimination of HCl or HBr that subsequently reacts at the M−B bond to provide the tungsten hydride and regenerate the haloborane catalyst (Scheme 4). An electrophilic addition of BI$_3$ to ferrocene has been observed,[42] and a recent structure of the product of addition of an alkyl dichloroborane to Cp$_2$WH$_2$, (*i*-PrBCl$_2$C$_5$H$_5$)CpPWH$_2$,[43] has been reported. This compound is analogous to the proposed intermediate in the haloborane-catalyzed rearrangements of the boryl complexes. The HCl remained incorporated in this product. Migration of coordinated boranes[44] and silyl

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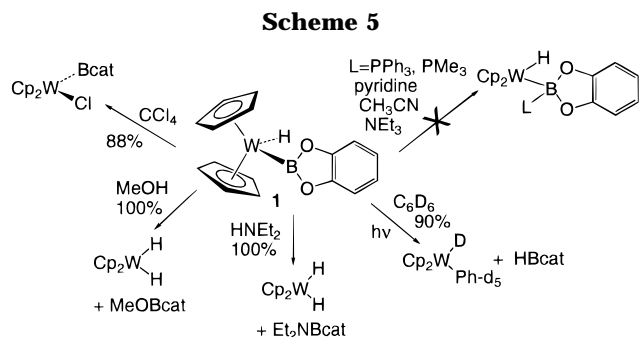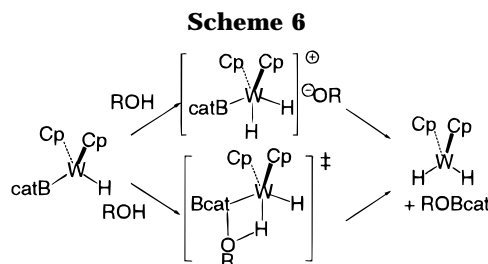(42) Ruf, W.; Fueller, M.; Siebert, W. *J. Organomet. Chem.* **1974**, *64*, C45−C47.
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Scheme 5

Scheme 6

groups to cyclopentadienyl ligands[45−47] have also been observed. The silyl migrations are believed to occur by migration to a deprotonated cyclopentadienyl ligand[46,47] formed in the presence of strong base or by an intramolecular migration triggered by an electronic effect of an accompanying halide ligand.[45] Perhaps the silyl migrations in the absence of base can also be accommodated by the mechanism in Scheme 4, with the metal halide and silyl groups generating catalytic amounts of chlorosilanes.

Reaction Chemistry of 1. A survey of the reactivity of complex **1** with small molecules is shown in Scheme 5. This chemistry includes photochemical reductive elimination, along with thermal reactions with halogen sources, with protic reagents, and with Lewis bases.

Halogenation. The boryl ligand was more stable than its accompanying hydride toward halogenation. Addition of 1 equiv of CCl_4 to **1** led to the formation of the chloroboryl complex $Cp_2W(Cl)(Bcat)$ (**4**) in 82% yield by NMR spectroscopy. Compound **4** was isolated in 60−80% yields as a brown powder by concentration of the reaction solution after 1 h and addition of pentane. Alternatively, this compound was crystallized from toluene/pentane solutions as dark brown, analytically pure, material.

Protonation. Reactions of compound **1** with proton donors are consistent with a strong W−B linkage and weak Lewis acidity. Amines react rapidly with haloboranes such as ClBcat as well as with the metallaborane $CpFe(CO)_2Bcat$. Reactions with B−H bonds such as those in catecholborane is slower, however. In contrast to rapid reactivity of amines with $CpFe(CO)_2Bcat$, the reaction of diethylamine with **1** showed complete and quantitative conversion to Et_2NBcat and Cp_2WH_2 only after warming at 45 °C for several hours. Moreover, attempts to conduct quantitative kinetic studies of this reaction led to the conclusion that this reaction of amine with **1** was catalyzed by trace amounts of water or catBOBcat. Our rate studies showed a large difference in rate depending on the water content of the solvent. Reaction rates varied by roughly 1 order of magnitude and were slowest when no hydrolysis of **1** was observed in the initial reaction solution. Addition of trace amounts of alcohol increased reaction rates with the amine, as did addition of catBOBcat.

Alcohols reacted essentially instantaneously with **1** to yield Cp_2WH_2 and the alkoxycatecholborane in quantitative yield by ^1H and ^{11}B NMR spectroscopy. Thus,

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rapid reaction of **1** with water would generate catBOBcat and Cp_2WH_2. We observed that catBOBcat reacts with diethylamine to generate water and 2 equiv of Et_2NBcat. The combination of these two reactions provides a water catalyzed pathway for addition of amines to **1**. Thus, **1** does not react directly with amines. Its weak Lewis acidity prevents direct N−H bond cleavage by either participation of the boron p-orbital in a four-centered transition state involving the amine N−H and metal complex W−B bond or precoordination of the amine to **1** through the amine lone pair.

Hydrido boryl complex **1** was more reactive to protic reagents than chloro boryl complex **4**. Addition of 0.1 equiv of MeOH to a 1:1 mixture of the two boryl complexes, followed by incremental additions of 0.2 equiv, showed relative reactivities of **1** to **4** that were roughly 2:1. This difference in reactivity can be attributed to either greater steric hindrance in **4** due to the larger Cl group or to increased π-bonding and decreased Lewis acidity in **4** due to the ability of the chloride to act as a π-donor into the same orbital that donates electron density into the boron p-orbital.[37]

However, the bis(boryl) compounds **2a,b** were also less reactive than **1** toward protic reagents. In contrast to the rapid reaction of **1** with alcohols, **2a,b** required several hours to react with ethanol and produce Cp_2WH_2 (60% yield, ^1H NMR with internal standard) and EtOBcat′ (67%). Confirming the more rapid reaction of **1** than **2b**, no hydridoboryl complex $Cp_2WH(Bcat′)$ was observed during the course of the reaction. The hydride signal for Cp_2WH_2 was the only hydride resonance observed near −12 ppm.

Thus, the greater reactivity of **1** over either **4** or **2b** must be rationalized on steric grounds, since the chloride and boryl ligands are opposite types of ligands. The chloride should be a weaker σ-donor than a boryl ligand, on the basis of the basicity of the two anions, and would act as a π-donor rather than π-acceptor. It has been shown that the site of protonation in $Cp*_2WH_2$ is the orbital located between the hydride ligands. Protonation at this portion of the molecules **1**, **4**, and **2** would have a dramatically reduced steric effect for protonation of **1**. Should protonation occur to the metal on the side of the boryl ligand opposite the ancillary covalent ligand, then the steric effect would be less pronounced. These arguments can be explained by the mechanisms in Scheme 6. Protonation would lead to an intermediate that does not undergo B−H reductive elimination, as is common for alkyl complexes, because of the strong metal−boryl bond.[29] Rather, the electrophilic boryl ligand, albeit weakly so, is subject to attack by the alkoxide anion, to produce the ethoxyborane and the tungsten hydride. This process can also occur in one step, with a four-centered transition state involving partial protonation and formation of the product by coordination of the lone pair to the boryl ligand.

Scheme 7
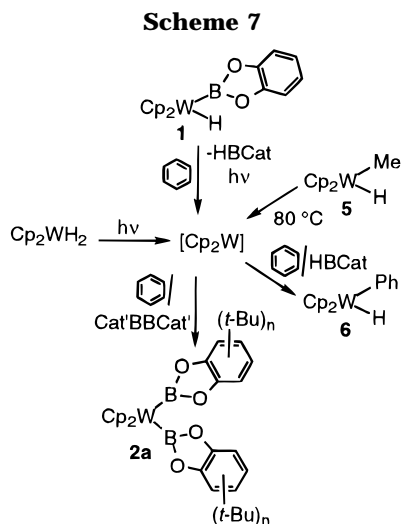
Potential Lewis Acid−Base Chemistry. Compound **1** was less Lewis acidic than catecholborane or *B*-chlorocatecholborane. Addition of Lewis bases such as PPh$_3$, PMe$_3$, NEt$_3$, pyridine, acetonitrile, or THF all led to no change in the ^{1}H or ^{11}B NMR spectrum of C$_6$D$_6$ solutions of **1**. Although catecholborane is less acidic than *B*-chlorocatecholborane, it does form a Lewis base adduct with pyridine.[48] Even in THF solvent or in the presence of excess pyridine, the ^{11}B NMR spectra of **1** were essentially identical to those in pure aromatic solvents. This reduced Lewis acidity can be attributed to the dπ−pπ bonding observed in the X-ray structure and to the increased steric hindrance due to the metallocene fragment.

Potential Insertion Chemistry. Boryl complex **1** was resistant to insertion chemistry. Addition of 1-hexene, 1-hexyne, CO, CO$_2$, and acetone led to no reaction with **1**. Compound **1** was also resistant to hydrogenolysis and exchange with boranes that were observed with CpFe(CO)$_2$BPh$_2$.[2] Studies concerning the π-bond strength and total bond energies for these compounds, as well as the chemistry of molybdenocene analogs that are likely to display more reactive M−B linkages, will be the subject of future reports.

Thermolysis and Photolysis. Consistent with the presence of haloborane initiating the rearrangement of **1**, pure samples of this boryl complex were extremely stable thermally. This compound did not undergo rearrangement or reductive elimination even after heating in toluene at 110 °C for 12 h in a sealed vessel. In contrast, compound **1** was photochemically reactive. A comprehensive view of the photochemical reactivity of the boryl complexes is given in Scheme 7. Irradiation of a C$_6$D$_6$ solution of **1** with a 450 W mercury arc lamp for only 10 min at room temperature led to 90% yield of HBcat and Cp$_2$W(D)(C$_6$D$_5$). These products of borane reductive elimination and solvent oxidative addition[49] were identified and quantified by ^{1}H, ^{2}H, and ^{11}B NMR spectroscopy. This chemistry was similar to that displayed by Cp$_2$WH$_2$, which is also thermally stable but photochemically labile.[49,50] However, compound **1** reacts much faster under identical photochemical conditions than does Cp$_2$WH$_2$.

This photochemical formation of catecholborane from **1** contrasts the formation of bis(boryl) complexes **2a,b** under photochemical conditions. Thus, we conducted experiments to determine the origins of this selectivity. The selectivity for B−B over C−H bond addition in the photolysis of Cp$_2$WH$_2$ in the presence of cat′BBcat′ and benzene was independent of whether tungstenocene was generated photochemically or thermally. Gentle thermolysis of [Cp$_2$W(H)(Me)] (**5**) is known to generate [Cp$_2$W].[49,51] Heating of **5** in benzene solvent for 4 h at 80 °C in the presence of 1−2 equiv of Cat′BBCat′ led to formation of **2a** in 70% yield. No Cp$_2$W(H)(Ph) (**6**) was observed during the course of the reaction, and **6** was stable in benzene solvent at 80 °C in the presence of cat′BBcat′. Therefore, Cp$_2$W(H)(Ph) could not be either a reaction intermediate or a kinetic product that is ultimately converted to a more stable bis(boryl) product.

The clean oxidative addition chemistry of diboron compounds led us to probe carefully for any potential oxidative addition chemistry of catecholborane by Cp$_2$W. Irradiation of Cp$_2$WH$_2$ for 6 h in benzene solvent containing HBcat (6 equiv) led to the solvent C−H activation product **6** rather than the borane addition product **1**. At short reaction times (30 and 60 min), however, we did observe small amounts (10−20% relative to **6**) of the B−H activation product **1**. The formation of this product in benzene medium does indicate that catecholborane addition is kinetically preferred over benzene addition. However, at longer reaction times the small amounts of boryl hydride **1** were converted to phenyl hydride **6**, as must occur given the photochemical lability of **1**. Unfortunately, we could not probe the selectivity of Cp$_2$W for B−H oxidative addition using methyl hydride **5** as a thermal precursor to tungstenocene because **5** reacted with catecholborane faster than it underwent reductive elimination to form tungstenocene.

The following series of photochemical stabilities results from these studies: [Cp$_2$W(Bcat′)$_2$] > [Cp$_2$W(Ph)(H)] > [Cp$_2$W(Bcat)(H)]. The selectivities by [Cp$_2$W] for B−B over C−H bond activation are precedented by the oxidative addition of diboron compounds with systems that do not undergo intermolecular C−H activation.[4,12,18,38,52,53] However, the final selectivity for C−H over B−H activation with Cp$_2$W contrasts the selectivities of systems that add the B−H bond of catecholborane but do not add the C−H bond of hydrocarbons.[14,54,55] Further, the resulting selectivity for B−B over B−H activation is exactly the opposite of the preference for C−H over unactivated and unstrained C−C bond activation, except in rare cases.[56−60]

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We have shown previously with an electron-rich, third-row system, albeit an iridium system,[15] that the metal−boron bond is stronger thermodynamically than the corresponding metal−hydride.[29] The stability of the tungsten bis(boryl) compound may be derived from a similar high bond dissociation energy of the metal−boron linkage. A kinetic effect that enhances selectivity for the boranes may result from the favorable matchup of the nucleophilic d^4 Cp$_2$W with the electrophilic diboron reagent.

Experimental Section

General Methods. Unless otherwise noted, all manipulations were carried out in an inert atmosphere glovebox or by using standard Schlenk or vacuum line techniques. ^{1}H NMR spectra were obtained on a GE QE 300 MHz or Ω 300 MHz Fourier transform spectrometer. ^{11}B, and ^{31}P spectra were obtained on the Ω 300 MHz Fourier transform operating at 96.38 and 121.65 MHz, respectively. ^{13}C NMR spectra were obtained on a GE QE 300 NMR spectrometer operating at 75.57 MHz. ^{1}H NMR chemical shifts were recorded relative to residual protiated solvent. Chemical shifts are reported in units of parts per million. Positive chemical shifts indicate resonances located downfield from TMS, 87% H$_3$PO$_4$, or BF$_3$·OEt$_2$ as external standards. Sealed NMR tubes were heated in Neslab constant-temperature baths.

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Catecholborane was distilled under vacuum prior to use. Diethylamine was dried over a small piece of sodium and was degassed before vacuum transfer. Carbon tetrachloride was degassed before use. Pentane (tech grade) was distilled under nitrogen from purple sodium/benzophenone ketyl made soluble by addition of tetraglyme to the still. Benzene, toluene, and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was vacuum transferred from CaH$_2$. Deuterated solvents for use in NMR experiments were dried as their protiated analogs but were vacuum transferred from the drying agent.

Cp$_2$W(H)(Bcat) (1). Li[Cp$_2$WH] (80−400 mg) that was prepared by deprotonation of Cp$_2$WH$_2$[30] was suspended in 5−10 mL of benzene. To this stirred solution was added dropwise at room temperature 0.9 equiv of chlorocatecholborane as a solution in 0.5−1 mL of benzene. The resulting solution was allowed to react at room temperature for 30 min, after which time the resulting yellow/orange suspension was filtered. The filtrate was concentrated to 1−2 mL and transferred to a small vial. Crystalline **1** was obtained by vapor diffusion of pentane into the concentrated benzene solution. Analytically pure **1** was obtained in 28−40% yield by this method. Alternatively, the reaction was run in toluene solvent. After reaction under the same conditions, the filtrate was concentrated to 1−2 mL and layered with pentane. Cooling to −35 °C for several days led to crystallization of **1** in 70% yield. However, these samples of **1** contained 5−10% of Cp$_2$WH$_2$ as impurity: ^{1}H NMR (C$_6$D$_6$) δ −10.47 (s, J_{W-H} = 53.4, 1H), 4.37 (s, 10H), 6.84 (m, 2H), 6.86 (m, 2H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 76.62 (s), 110.66 (s), 121.06 (s), 151.61 (s); ^{11}B NMR (C$_6$D$_6$) δ 57.2; IR (Et$_2$O) 1952. Anal. Calcd for C$_{16}$H$_{15}$BO$_2$W: C, 44.28; H, 3.48. Found: C, 44.69; H, 3.86.

Synthesis of Cp$_2$W(Bcat-4-*t*-Bu)$_2$ (2a). A solution of Cp$_2$WH$_2$ (42.0 mg, 0.133 mmol) was dissolved in C$_6$H$_6$ (4 mL), and the solution was added to a vial containing 1.0 equiv (49.5 mg) of (*t*-Bu-C$_6$H$_3$O$_2$B)$_2$. The solution was divided into four NMR sample tubes, and the tubes were placed 1.0 in. from the photolysis lamp and irradiated for 3.5 h. ^{11}B NMR spectra taken periodically showed that this reaction time was neces-

sary for complete reaction. The samples were then brought into the drybox, the solutions were combined, and the volume was reduced to 0.5 mL. This benzene solution was layered with pentane to afford yellow crystals of **2b** that were suitable for X-ray diffraction analysis: yield 52 mg (57%); ^{1}H NMR (C$_6$D$_6$) δ 7.13 (d, 2.0 Hz, 1H), 6.93 (d, 8.2 Hz, 1H), 6.73 (dd, 8.2 Hz, 2.0 Hz, 1H), 4.70 (s, 10H), 1.16 (s, 9H); ^{11}B NMR δ 59.3; ^{13}C{^{1}H} NMR δ 151.19, 149.14, 143.69, 117.2, 109.5, 108.27, 81.59, 34.42, 31.86.

Synthesis of Cp$_2$W(Bcat-3,5-di-*t*-Bu)$_2$ (2b). Preparative Scale. A solution of Cp$_2$WH$_2$ (31.0 mg, 0.0981 mmol) was dissolved in toluene (3 mL) and placed into an NMR sample tube. The tube was placed 1 in. from a the photolysis lamp and was irradiated for 3.5 h. The sample was then brought into the drybox, the solutions were combined, and the volume was reduced to 0.5 mL. This toluene solution was layered with pentane and cooled to −35 °C to afford analytically pure, yellow crystals of **2b**: yield 35 mg (45%); ^{1}H NMR (C$_6$D$_6$) δ 7.07 (s, 1H), 7.00 (s, 1H), 4.711 (s, 10H), 1.50 (s, 9H), 1.25 (s, 9H); ^{11}B NMR δ 58.2; ^{13}C{^{1}H} NMR δ 151.28, 146.81, 143.13, 132.00, 114.10, 106.46, 81.61, 34.81, 34.38, 32.06, 29.99. Anal. Calcd for C$_{38}$H$_{50}$B$_2$O$_4$W·C$_7$H$_7$: C, 62.31; H, 6.62. Found: C, 62.08; H, 6.64.

Small Scale To Obtain Crude Reaction Yield. A solution of Cp$_2$WH$_2$ (4.2 mg, 0.0133 mmol) was dissolved in C$_6$H$_6$ (0.5 mL), and the solution was added to a vial containing roughly 0.5 mg of 1,3,5-(MeO)$_3$C$_6$H$_3$ and exactly 1.0 equiv (4.9 mg) of (*t*-Bu-C$_6$H$_3$O$_2$B)$_2$. The solution was placed into an NMR sample tube, and an initial ^{1}H NMR spectrum was obtained. The tube was placed 1 in. from the photolysis lamp and was irradiated for 3.5 h. The final ^{1}H NMR spectrum showed formation of **2b** in 92% yield.

X-ray Structural Determination of 1 and 2a. Data Collection. A pale yellow rectangular plate crystal of **1** having approximate dimensions of 0.10 × 0.10 × 0.12 mm or **2a** having approximate dimensions of 0.08 × 0.10 × 0.12 was mounted in a glass capillary (for **1**) or on a glass fiber (for **2a**). All measurements were made on an Enraf-Nonius CAD4 diffactometer with graphite-monochromated Mo Kα radiation.

Cell constants and an orientation matrix for data collection obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 17.00° < 2θ < 29.00° for **1** and 10.30 < 2θ < 18.00° for **2a** corresponded to a monoclinic cell with dimensions a = 10.161-(1) Å, b = 10.597 Å, c = 13.242(2) Å, β = 100.023(8) Å, and V = 1404.1(5) Å^3 for **1** and a = 14.829(4) Å, b = 7.976(2) Å, c = 27.282(5) Å, β = 98.76(2)°, and V = 3189(2) Å^3 for **2a**. For Z = 4 and M_r = 432.95 the calculated density is 2.048 g/cm^3 for **1** and for M_r = 742.18 the calculated density is 1.546 g/cm^3 for **2a**. On the basis of the systematic absences of $h0l$, $h + 1$ = $2n + 1$, and $0k0$, $k = 2n + 1$, and the successful solution and refinement of the structure, the space group was determined to be $P2_1/n$ (No. 14) for **1**. On the basis of the systematic absences of $h0l$, $h + 1 = 2n + 1$, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P2/n$ (No. 13) for **2a**.

The data were collected at a temperature of 23 ± 1 °C for **1** and −119 ± 5 °C for **2a** using the 2θ/ω scan technique to a maximum 2θ value of 49.9° for **1** and 52.6° for **2a**. ω scans of several intense reflections made prior to data collection had an average width at half-height of 0.31° with a take-off angle of 2.8°. Scans of (0.80 + 0.35 tan θ)° for **1** and (0.53 + 1.10 tan θ)° for **2a** were made at variable speeds ranging from 1.0 to 5.5 deg/min (in ω) for **1** and from 1.0 to 16.5 deg/min (in ω) for **2a**. Moving crystal moving counter background measurements were made by scanning an additional 25% above and below the scan range. The counter aperture consisted of a variable horizontal slit with a width ranging from 2.0 to 2.5 mm and a vertical slit set to 2.0 mm. The diameter of the incident beam collimator was 1.3 mm for **1** and 0.8 mm for **2a**, and the crystal to detector distance was 21 cm for both.

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For intense reflections an attenuator was automatically inserted in front of the detector.

Data Reduction, Structure Solution, and Refinement. Of the 2770 reflections which were collected for **1**, 2641 were unique (R_{int} = 0.033). Of the 7198 reflections which were collected for **2a**, 6929 were unique (R_{int} = 0.078). The intensities of the two representative reflections which were measured after every 60 min of X-ray exposure time declined by −50.00% for **1** but were constant for **2a**. A linear correction factor was applied to the data to account for this phenomena with **1**, but no correction was applied for **2a**. The linear absorption coefficient for Mo Kα was 84.0 cm^{-1} for **1** and 37.3 cm^{-1} for **2a**. For **1** an empirical absorption correction using the program DIFABS was applied, which resulted in transmission factors ranging from 0.60 to 1.57. The data were corrected for Lorentz and polarization effects. For **2a**, an empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.77 to 1.00. The data were corrected for Lorentz and polarization effects.

The structures were solved by the Patterson method.[61] This procedure revealed the position of the W atoms, and subsequent difference maps revealed the remaining atoms. The non-hydrogen atoms were refined anisotropically. The thermal parameters of the carbon atoms on each cyclopentadienyl ring of **1** were somewhat larger than normal. The hydrogen atoms were included in calculated positions. In the case of the methyl group hydrogens of **2a**, one hydrogen atom was located in the difference map and included in an idealized position to set the orientation of the other two hydrogen atoms. For **1**, the final cycle of full-matrix least-squares refinement was based on 1456 observed reflections ($I > 3.00\sigma(I)$), with 181 variable parameters, and converged (the largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.039$ and $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|)]^{1/2} = 0.039$. For **2a**, the final cycle of full-matrix least-squares refinement was based on 4244 observed reflections ($I > 3.00\sigma(I)$), with 388 variable parameters, and converged (the largest parameter shift was 0.001 times its esd) with unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.041$ and $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|)]^{1/2} = 0.050$.

The standard deviation of an observation of unit weight was 1.42 for **1** and 1.69 for **2a**. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$ reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.38 (located 1.77 Å away from the W atom) and −1.30 e/Å^3 for **1** and 1.29 (located 1.04 Å from the W atom) and −2.71 e/Å^3. Neutral atom scattering factors were taken from Cromer and Waber.[62] Anomalous dispersion effects were included in F_c; the values for $\Delta f'$ and $\Delta f''$ were also those of Cromer and Waber.[63] All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corp.

Cp(C₅H₄BPh₂)WH₂ (3a). Li[Cp₂WH] (80 mg) that was prepared by deprotonation of Cp₂WH₂[30] was suspended in 5−10 mL of toluene. To this stirred solution was added dropwise at room temperature 0.9 equiv of BrBPh₂ as a solution in 0.5 mL of toluene. The resulting solution was allowed to react at room temperature for 30 min, after which time the resulting yellow/orange suspension was filtered. The filtrate was concentrated to 1−2 mL and transferred to a small vial. The sample was layered with pentane, and **3b** was obtained in 60% yield (65 mg) as spectroscopically pure

material. This material was recrystallized before submitting for microanalysis: ¹H NMR (C₆D₆) δ −10.09 (s, d; J_{W-H} = 72.5 Hz, 2H, W−H), 3.88 (m, 2H, C₅H₄BPh₂), 4.08 (s, 5H, Cp), 4.75 (m, 2H, C₅H₄BPh₂), 7.20 (t, 7.0 Hz, 2H, BPh₂), 7.25 (t, 7.3 Hz, 4H, BPh₂), 7.81 (d, J = 7.2 Hz, BPh₂); ¹¹B NMR (C₆D₆) δ 41; ¹³C{¹H} NMR (C₆D₆) δ 77.34, 78.63, 85.22, 127.37, 127.43, 134.83; the quaternary carbons bound to boron could not be observed. Anal. Calcd for C₂₂H₂₁BW: C, 55.04; H, 4.41. Found: C, 54.77; 4.33.

Cp(C₅H₄Bcat)WH₂ (3b). From Li[Cp₂WH]. A procedure identical to preparation of **1** in toluene solvent was followed except that 1.2 equiv of chlorocatecholborane was used and the solution was left to react overnight. Recrystallization from toluene/pentane solutions gave **3a** in 21% yield as a pale yellow solid: ¹H NMR (C₆D₆) δ −11.31 (s, d; J_{W-H} = 72 Hz; 2H, W−H), 4.14 (s, 5H, Cp), 4.23 (t, J = 2.1 Hz, 2H, C₅H₄Bcat), 4.59 (t, J = 2.1 Hz, 2H, C₅H₄Bcat), 6.73 (m, 2H, Bcat), 6.98 (m, 2H, Bcat); ¹¹B NMR (C₆D₆) δ 33; ¹³C{¹H} NMR (C₆D₆) δ 73.82, 74.23, 80.23, 111.97, 122.16, 148.81. Anal. Calcd for C₁₆H₁₅BO₂W: C, 44.29; H, 3.48. Found: C, 43.77; H, 3.71.

From Reaction of 1 with a Catalytic Amount of Chlorocatecholborane. Compound **1** (6.0 mg, 0.014 mmol) was dissolved in 0.6 mL of C₆D₆. C₆H₅(t-Bu) (1−2 mg) was added as an internal standard, and the sample was transferred to an NMR tube equipped with a Teflon-lined screw cap. An initial ¹H NMR spectrum was obtained to determine the ratio of **1** to internal standard. Chlorocatecholborane (ca. 0.2 mg, 10 mol %) was weighed into a vial, and the sample of **1** in C₆D₆ was added to the vial. The resulting sample was returned to the NMR tube and was warmed to 45 °C for 2 h. A second ¹H NMR spectrum showed complete consumption of **1** and formation of **3a** in 82% yield as determined by integration of the cyclopentadienyl resonance versus the internal standard.

Cp₂W(Cl)(Bcat) (4). Preparative Scale. To a solution of **1** (65 mg, 0.15 mmol) in 5 mL of toluene was added 1.0 equiv of CCl₄ by syringe. The solution turned immediately dark brown. Addition of pentane to the reaction solution precipitated **4** as a brown powder (55 mg, 78%) that was roughly 90% compound **4** as determined by ¹H NMR spectroscopy. Alternatively **4** was prepared as dark brown analytically pure crystals by concentrating the toluene reaction solution and cooling to −35 °C. Once isolated, this compound was not soluble enough in hydrocarbon solvents to obtain satisfactory signal to noise ratios for ¹³C NMR spectra and decomposed slowly in methylene chloride solvent: ¹H NMR (C₆D₆) δ 4.49 (s, 10H), 6.88 (m, 2H), 7.24 (m, 2H); ¹¹B NMR (C₆D₆): δ 49. Anal. Calcd for C₁₆H₁₄BClO₂W: C, 41.30; H, 3.01. Found: C, 41.29; H, 3.03.

Small-Scale Reaction for NMR Yield Determination. Compound **1** (4.0 mg) was dissolved in C₆D₆ solvent (0.6 mL), C₆H₅(t-Bu) (1−2 mg) was added as an internal standard, and the sample was transferred to an NMR tube equipped with a Teflon-lined screw cap. An initial ¹H NMR spectrum was obtained to determine the ratio of **1** to internal standard. A 1 equiv amount of CCl₄ was added, and a second ¹H NMR spectrum was obtained that showed complete reaction of **1** and formation of **4** in 88% yield as determined by integration of its cyclopentadienyl resonance versus the internal standard.

Photolysis of 1. A 5.2 mg (0.012 mmol) amount of **1** was dissolved in 0.6 mL of C₆D₆. C₆H₅(t-Bu) (1−2 mg) was added as an internal standard, and the sample was transferred to an NMR tube equipped with a Teflon-lined screw cap. An initial ¹H NMR spectrum was obtained to determine the ratio of **1** to internal standard. The sample was then placed approximately 2 cm from a 150 W medium-pressure Hanovia mercury arc lamp located in a water-cooled Pyrex immersion well. The sample was irradiated for 20 min at room temperature, and a second ¹H NMR spectrum was obtained. All of **1** had been consumed. Catecholborane and Cp₂W(D)(C₅D₅) was formed in 88% and 90% yields, as determined by comparison of the ratio of integrals for the two products versus the internal

(61) Calabrese, J. C. Ph.D. Thesis, Wisconsin−Madison, 1972.
(62) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2A.
(63) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

standard. Catecholborane was also identified by its characteristic doublet resonance at δ 28 in the ^{11}B NMR spectrum.

Reaction of 1 with Ethanol. Compound **1** (6 mg) was dissolved in C_6D_6 solvent (0.6 mL), C_6H_5Me (1–2 μl) was added as an internal standard, and the sample was transferred to an NMR tube equipped with a Teflon-lined screw cap. An initial ^1H NMR spectrum was obtained to determine the ratio of **1** to internal standard. A 1 equiv amount of EtOH was added, and a second ^1H NMR spectrum was obtained that showed complete reaction of **1** and formation of Cp_2WH_2 and EtOBcat in quantitative yields as determined by integration of the cyclopentadienyl resonance and ethoxy methylene resonance versus the internal standard. EtOBcat was also identified by its ^{11}B NMR resonance at δ 22.

Kinetic Measurements of the Reaction of 1 with Diethylamine. A 2 mL volumetric flask was charged with 8–10 mg of **1** and C_6D_6. This solution (0.62 mL) was transferred to an NMR tube equipped with a Teflon-lined screw cap. The desired amount of diethylamine was added by syringe, typically 10 μL. This sample was then placed in the NMR spectrometer that was warmed to either 45 or 55 °C. An automated data acquisition program acquired single-pulse ^1H NMR spectra at designated intervals. The decay of **1** was determined by the decay of the integral values for the cyclopentadienyl resonance of **1**. The yields of products, as determined by comparison of the integrations to the initial spectrum, were shown to be consistently quantitative. Linear first-order plots were obtained in all cases, but rate constants varied by a factor of 2–3 depending on the batch of **1** and the batch of solvent brought into the drybox after vacuum transfer from a purple sodium/benzophenone ketyl.

Reaction of 1 with Potential Lewis Bases. Samples of **1** (3–6 mg) in C_6D_6 solvent were treated with 10 equiv of PMe_3, PPh_3, pyridine, acetonitrile, and triethylamine. The resulting samples were placed into NMR tubes and analyzed by ^1H NMR spectroscopy and ^{11}B NMR spectroscopy. No changes were observed from samples of pure **1** in C_6D_6.

Reaction of 2a with EtOH. A 5.3 mg (7.7 mmol) amount of **2a** was weighed into a vial and was dissolved in 0.6 mL of C_6D_6. Roughly 0.5 mg of 1,3,5-$(MeO)_3C_6H_3$ was added as an internal standard, and the solution was placed in a rubber septum-capped NMR tube. A ^1H NMR spectrum was obtained and integrated. An excess of EtOH (1.0 μL 17 mmol) was then added. ^1H NMR spectra taken periodically indicated that the reaction required more than 2 h for completion and that Cp_2WH_2 was formed in 60% yield, while EtOBcat′ was formed in 67% yield.

Supporting Information Available: Tables of positional parameters, U values, intramolecular distances, intramolecular bond angles, Cartesian coordinates, and torsion angles for **2a** (15 pages). Ordering information is given on any current masthead page. X-ray data have been provided previously for **1**.[3]

OM9606303